Nanocrystalline Copper Selenide Photoeletrode used in Photoelectrochemical Solar Cells

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Abstract

The development of thin film solar cell is an active area of research . Nanocrystalline thin films of copper selenide have been grown on glass and indium tin oxide (ITO) substrates using chemical method. At different deposition time , golden films have been synthesized and annealed at 200^{0}C for 2H and were examined by means AFM micrographs for their structural and morphological properties. Average spherical grains of the order of ***25.49*** *nm to* ***34.06****nm for different deposition time and size aggregated over about 120 ± 10 nm for different deposition time islands were seen by AFM images. Conductivity in copper selenide thin films make it a suitable candidate for solar cells. Their photoelectrochemical performance was investigated in standard two electrode configuration with redox electrolyte. The investigation may be useful in obtaining efficient, non polluting, stable and low cost solar cell to compete with the existing technology.*

Keywords: *Copper selenide, thin films,Photoelectrochemical cells,AFM , Surface morphology.*

Introduction

Solar energy source is only long term natural source of energy. The photo electrochemical cells are considered as potential energy source for future. The photo electrochemical cell (PEC) is an attractive means of converting solar energy into electricity. It is considered a major candidate for obtaining energy from the sun, since it can convert sunlight directly into electricity. It can provide nearly permanent power and is virtually free of pollution.The low-temperature processes which enables formation of thin films onto glass substrates in addition to the conducting films of indium tin oxide substrate (ITO) which can potentially lead to a new generation of photovoltaic devices that are light in weight, foldable, flexible and moldable. Copper selenide has been studied with great interest during the past decades because of its potential application in the fabrication of photovoltaic devices. The inorganic thin films of copper selenide is focused in this work by direct chemical deposition method and annealed at 200^{o}C for 2 hour for crystalline improvement.

The films are developed as photoelectrode in the photoelectrochemical cell, an aqueous solution of polysulphide serves as a redox couple to maintain the stability of the copper selenide photo electrodes. The copper selenide electrode exhibited photo-activity in polysulphide electrolyte towards positive polarity. The fact that the photocurrent occurs on the negative (cathode) potential area indicates that the films prepared are of p-type (positive).

The PV effect using nanocrystalline thin film on indium tin oxide substrate (ITO) as Photoelectrode in PEC cell has been discribed .The thin films of CuSe on glass substrate were characterized for their structural, surface morphological atomic force microscopy (AFM) .

Experimental Details:

1 .1Preparation of nanocrystalline CuSe thin Film:

Nanocrystalline thin films of copper-selenide are grown on glass and indium doped tin oxide substrates using chemical method. The photoelectrode are prepared for different deposition time of 60min, 90min, 120 min and 180 min at temperature 45^{0}c and golden films are deposited. The samples of thin film are annealed at 200ºC for 2 hour in oven.

1.2 Reaction mechanism

It is well known that sodium selenosulphate hydrolyzes in alkaline medium to give Se^{2-} ions as

$Na_2SeSO_3 + OH^- \rightarrow Na_2SO_4 + HSe^-$ **(1)**

$2HSe^- + 2OH^- \rightarrow 2H_2O + Se^{2-}$ **(2)**

In presence of Cu^{2+} ions in the bath, copper selenide is formed if the ionic product of Cu^{2+}, Se^{2-} exceeds the solubility product of copper selenide. The formation of particular phase such as Cu_2Se, Cu_2Se_3, $Cu_{2-x}Se$ will be governed by copper ion concentration, deposition temperature, rate of release of Cu^{2+} from the tartaric acid complex as facilitating the desired ion transport .

A reaction vessel containing glass and indium doped tin oxide (ITO) substrates was used in the experiment. For preparation of sodium salenosulfite (Na_2SeSO_3) first of all 100ml aqueous solution of sodium sulfite (1M) are prepared, then 0.1M of selenium powder are added with constant stirring, the mixture are heated to 60ºc till the selenium is dissolved in the solution. Upon filtration, sodium salenosulfite solution are obtained. The reaction vessel was filled with the composition of solution: 0.1 M 50 ml $CuSO_4$ + 1 M, 2 ml tartaric acid and 0.1M 6 ml Na_2SeSO_3 solution. The glass slides were cleaned with a suitable cleanser, scrubbed with soft cotton, washed thoroughly with de-ionized water followed by rinsing and drying in air. These glass and ITO coated sides were used as substrates for deposition, which were fixed to the circular holder(figure 1) .The temperature of reaction solution was kept as 45ºc during the deposition.

figure-(1) Experimental setup for preparation of photoelectrode

The ITO side was kept facing towards the solution and allowed to rotate with a speed of **25** rpm. The thermostat was set to a temperature of **45ºC** and the reaction was carried out for **60** min, **90** min, **120** min and **180** min with constant stirring of the solution throughout the experiment. Good golden adherent films were deposited onto both glass and ITO substrates.

The configuration of PEC cell is a single glass vessel surrounded by dark, using CuSe nanocrystalline film on ITO substrate as photo anode, graphite as counter electrode and polysulphide solution(using Sulpher-**S**, **NaOH,** **Na_2S**) as electrolyte.Photo-electrochemical (PEC) performance of copper selenide film was studied . The distance between working electrode and counter electrode was kept 1 cm. Photocurrent–voltage (I–V) performances of annealed copper selenide photo electrodes were measured under dark and 315 lux light illumination intensity.

Result & Conclusions.

2. Photovoltaic characteristics:

An experimental setup for evaluation of I-V characteristics is established as shown in figure 2. In this experiment the light source is kept at distance of 10 centimeter from beaker which resulted the intensity of **315 lux** as measured by standard lux meater . There after value of resistance is varied and different values of voltage and current are measured and noted to plot graph between current and voltage .

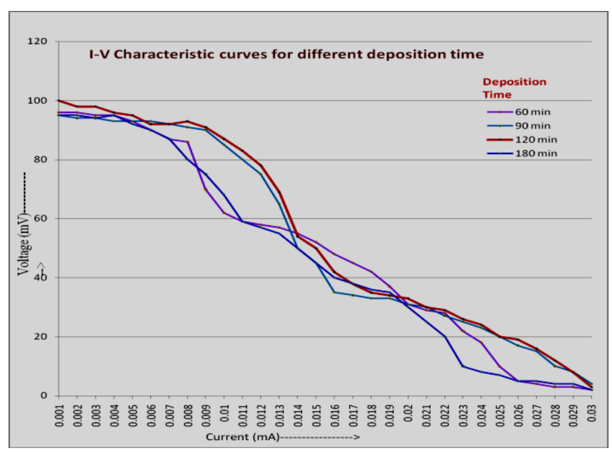


Figure-2. (I-V characteristics of PEC solar cells for photo electrodes prepared at different deposition time)

Figure 1shows I-V characteristics of PEC cells having photoelectrodes prepared for different deposition time. Observations show that as load is reduced there is increase in output current and output voltage decreases. Copper selenide is studied with great interest during the past decades because of its potential application in the fabrication of photovoltaic devices. The I–V characteristics of solar cell is plotted for four different electrodes.The deposition time of CuSe for each anode is kept different ,viz. 60 min., 90 min,120 min and 180 min. The light illumination used is 315 lux intensity and polysulphide solution serves as a redox to maintain the stability of the copper selenide photoelectrodes.

3.Atomic Force Microscopy (AFM):

The atomic force microscope (AFM) is ideally suited for characterizing nanoparticles. Using the Atomic Force Microscope (AFM), individual particles and groups of particles can be resolved. It offers the capability of 3D visualization and both qualitative and quantitative information on many physical properties including size, morphology, surface texture and roughness. Statistical information, including size, surface area, and volume distributions, can be determined as well. The AFM offers visualization in three dimensions. Resolution in the vertical, or Z, axis is limited by the vibration environment of the instrument, where as resolution in the horizontal, or X-Y, axis is limited by the diameter of tip utilized for scanning.

For finding the results of Atomic Force Microscopy (AFM) studies of CuSe deposited thin film on glass plate, **AFM (NTMDT)** instrument is used. (instrument name given by Center of Nanoscience & Nanotechnology, Sathyabama University" Chennai) **.**The goal is to determine the shape, size and size distribution of nanoparticles. CuSe thin film are prepared on glass substrate for deposition time 60 min 120 min & 180 min and characterized them by AFM in the dynamic mode.

(a)Atomic force microscopic image analysis of CuSe thin film for deposition time 60 min.

Fig. 3.1shows 2D atomic force microscopic image of CuSe thin film for deposition time 60 min. There was agglomeration of particles in most of the cases as evident from the 3D image (Fig.3.2). The difference between the lowest and highest points on the surface is 40 nm for scans over 2.5x2.5 μm for sample.

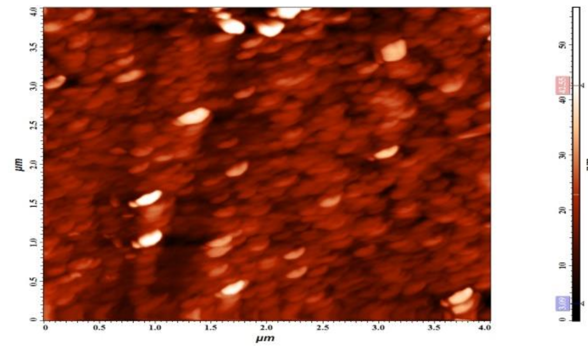


Fig.3.1-2D Image (Deposition time -60 min.)

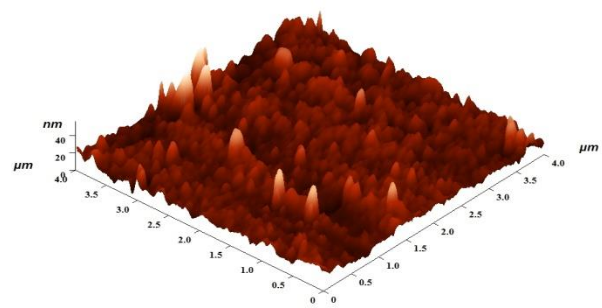


Fig.3.2 -3D Image (Deposition time -60 min.)

(B) Atomic force microscopic image analysis of CuSe thin film for deposition time 120 min.

Fig. 3.3 shows 2D atomic force microscopic image of CuSe thin film for deposition time 120 min. There was agglomeration of particles in most of the cases as evident from the 3D image (Fig.3.4). The difference between the lowest and highest points on the surface is 120 nm, scans over 2.5x2.5 μm for sample.

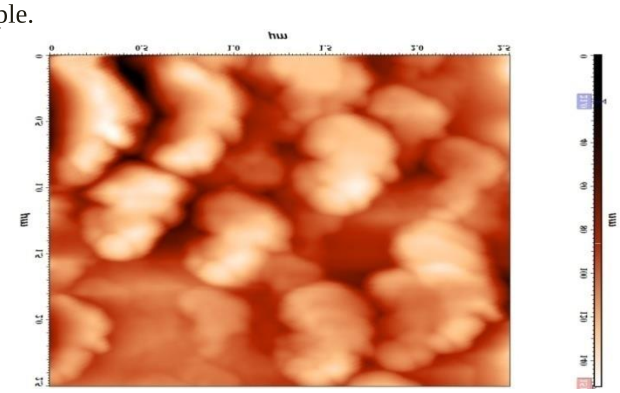


Fig.3.3-2D Image (Deposition time -120 min.)

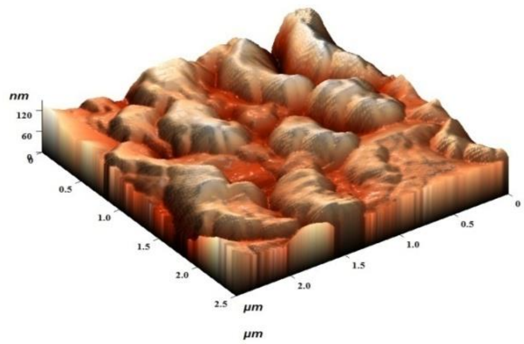


Fig.3.4 - 3D Image (Deposition time -120 min.)

(C)Atomic force microscopic image analysis of CuSe thin film for deposition time 180 min.

Fig. 3.5 shows 2D and Fig.3.6 shows 3D atomic force microscopic image of CuSe thin film for deposition time 180 min. The difference between the lowest and highest points on the surface is 160 nm, scans over 2.5x2.5 μm for sample.

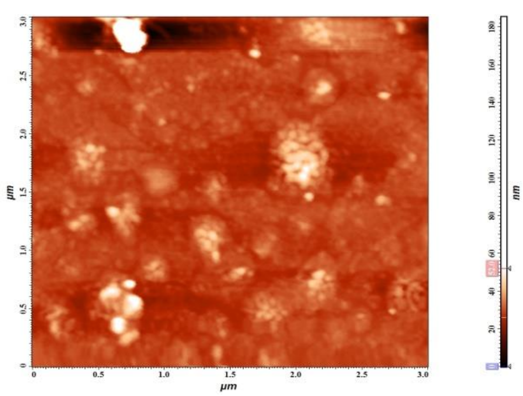


Fig.3.5 -2D Image (Deposition time -180 min.)

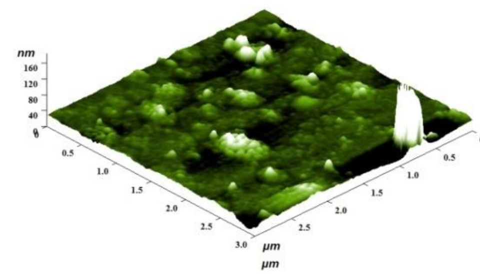
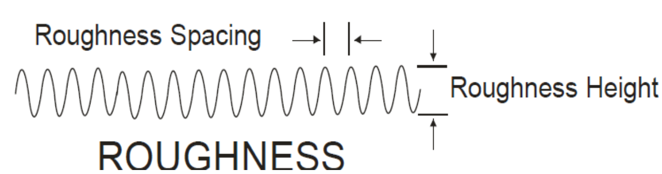


Fig.3.6-3D Image (Deposition time -180 min.)

This shows that as the deposition time is increased the difference between highest and lowest points increases, which indicates that deposition is fevered at higher elevated parts rather then the lower parts on the film and surface becomes more and more uneven.

3.1.Roughness Analysis :

Roughness is often described as closely spaced irregularities or with terms such as 'uneven', 'irregular', 'coarse in texture', 'broken by prominences', and other similar ones . Similar to some surface properties such as hardness, the value of surface roughness depends on the scale of measurement. In addition, the concept of roughness has statistical implications as it takes into consideration factors such as sample size and sampling interval. It is quantified by the vertical spacing of a real surface from its ideal form. If these spacing are large, the surface is rough; if they are small the surface is smooth.



The roughness can be characterized by several parameters and functions (such as height parameters, wavelength parameters, spacing and hybrid parameters (Gadelmawla et al., 2002). The following parameters and functions related to the height and spacing (also called parameters R and S) will be discussed as well as their calculation.

a-Height parameters (R)

The most significant parameters in the case of roughness are the Height Parameters.

b- Roughness average

Among Height Parameters, the roughness average (Ra) is the most widely used because it is a simple parameter to obtain when compared to others. The roughness average is described as follows (Park, 2011).

$$R_a = \frac{1}{L}\int_0^L |Z(x)|\,dx$$

Where Z(x) is the function that describes the surface profile analyzed in terms of height (Z) and position (x) of the sample over the evaluation length “L” .Thus, the Ra is the arithmetic mean of the absolute values of the height of the surface profile Z(x). Many times the roughness average is called the Arithmetic Average (AA), Center Line Average (CLA) or Arithmetical Mean Deviation of the Profile. The average roughness has advantages and disadvantages. The advantages include: ease of obtaining the same average roughness of less sophisticated instruments, for example, a profilometer can provide (Ra); possibility of repetition of the parameter, since it appears very stable statistically, recommended as a parameter for the characterization of random surfaces, it is usually used to describe machined surfaces. Fig.3.7 Profile of a surface (Z) represents the average roughness Ra and Rq is the RMS roughness based on the mean line.

$$R_q = \sqrt{\frac{1}{L}\int_0^L |Z^2(x)|\,dx}$$

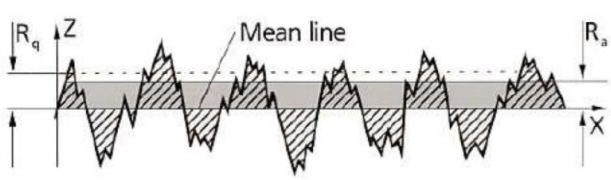


Fig.3.7- Profile of a surface (Z)

The average roughness, as already said, is just the mean absolute profile, making no distinction between peaks and valleys. Thus it becomes a disadvantage to characterize an average surface roughness if these data are relevant.

The average roughness can be the same for surfaces with roughness profile totally different because it depends only on the average profile of heights. Surfaces that have different undulations are not distinguished . We may have an even surface and some other with peaks (or valleys) with small contributions presenting the same value of average roughness. For this reason, more sophisticated parameters can be used to fully characterize a surface when more significant information is necessary, for example, distinguish between peaks and valleys.

c- Root mean square roughness (Rq)

The root mean square (RMS) is a statistical measure used in different fields. We cite, as an example, the use of the RMS amplitude applied to harmonic oscillators, such as on an alternating electric current. The root mean square of roughness (Rq) is a function that takes the square of the measures. The RMS roughness of a surface is similar to the roughness average, with the only difference being the mean squared absolute values of surface roughness profile. The function Rq is defined as (Gadelmawla et al., 2002):

$$R_q = \sqrt{\frac{1}{L}\int_0^L |Z^2(x)|\,dx}$$

Roughness analysis: Table-[A]

Parameters	Dep.time -60 min	Dep.time -120 min	Dep.time-180 min
Amount of sampling	**65536**	**65536**	**65536**
Height parameters Max	**56.6414 nm**	**151.68 nm**	**185.092nm**
Height parameters min.	**0 nm**	**0 nm**	**0 nm**
Root mean square roughness (Rq)	**4.99183 nm**	**18.6622 nm**	**7.57602 nm**
Peak-to-peak, Sy	**56.6414 nm**	**151.68 nm**	**185.092 nm**
Ten point height, Sz	**28.3207 nm**	**76.0522 nm**	**87.2532 nm**
Average wavelength	**27.3955 nm**	**104.161 nm**	**89.4877 nm**
Average Roughness (Ra)	**3.49004 nm**	**14.6218 nm**	**3.12743 nm**

***(**All above values of Parameters is given by Center of Nanoscience & Nanotechecnology, Sathyabama University" Chennai)

From roughness analysis table-[A] , it is observed that average roughness for 60, 120, &180 min deposition time is **3.49004 nm , 14.6218 nm, 3.12743 nm** respectively.ie roughness is maximum with deposition time 120 min ,but roughness decrease for 180 min deposition time because amount of deposited CuSe increase and smoothness of CuSe thin film increase.

References

1. K.Gour, P.Pathak el. (2018) International Journal of Research and Analytical Reviews Vol.5,Issue 4.
2. K.Gour, P.Pathak el. (2017). International Journal of Scientific Engineering and Research (IJSER) (ISSN:2347-3878) Vol.5,Issue 7.
3. Swapnil B. Ambade , R.S. Mane , S.S. Kale , S.H. Sonawane , Arif V. Shaikh , Sung-Hwan Han(2006) Applied Surface Science 253 ,2123–2126
4. **Nanocharacterisation, (**2007) Augus I Kirkland and John L Hutchison, ISBN: 978-0-85404-241-8 RSC, The Royal Society of Chemistry UK,
5. E.S. ***Gadelmawla et al***. (***2002***) Journal of Materials Processing Technology 123 133±145.
6. SeJin Ahn, Sunghun Jung, Jihye Gwak, Ara Cho, Keeshik Shin, Kyunghoon Yoon, Doyoung Park , (2010)APPLIED PHYSICS LETTERS **97**, 021905
7. Ezenwa I. A., Okereke N. A. and Okoli L. N.IPASJ (2013)International Journal of Electrical Engineering (IIJEE) Volume 1, Issue 6, ISSN 2321-600X
8. A.E.-H.B. Kashyout, E.-Z. Ahmed , T. Meaz , M. Nabil , M. Amer , , (2014) Alexandria Engineering Journal 53, 731–736,
9. S.Martin,C.Guillen, (2011) Energy Procedia 10 182 – 186
10. G. Juška , V. Gulbinas , and A. Jagminas ,Lithuanian (2010) Journal of Physics, Vol. **50**, No. 2, pp. 233–239
11. Bart Vermang , Jörn TimoWätjen , Viktor Fjällströma, Fredrik Rostvall , Marika Edoff (2014) Thin Solid Films
12. Xuewen Wang, Yuan Zhang, Zhouhu Deng, Yujue Wang, Zidong Wang, I. Shih, Journal of Crystallization Process and Technology, 2012, 2, 142-145
13. Peng Huang • Yifei Kong • Zhiming Li •Feng Gao • Daxiang Cui, NANO EXPRESS Nanoscale Res Lett 5:949–956 (2010)
14. Ezenwa I.A, Okereke N.A and Okoli L.N, , (2013).International Research Journal of Engineering Science, Technology and Innovation (IRJESTI),(ISSN-2315-5663) Vol. 2.
15. A.Hemati, S. Shrestha, M. Agarwal, and K. Varahramyan(2012) , Journal of Nanomaterials,Volume Article ID 512409.
16. Okereke, N.A. and Ekpunobi (2011),Research Journal of Chemical Sciences ,ISSN 2231-606X Vol. 1(6), 64-70, Sept.